

## V.G.4 PEM Fuel Cell Durability

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direction determined annually by DOE

### Objectives

Identify and quantify factors that limit proton exchange membrane (PEM) fuel cell durability:

- Define degradation mechanisms
- Measure property changes of fuel cell components from operation
  - Life testing of materials
    - Examine testing conditions, including drive cycle
  - Structural changes of membrane electrode assembly (MEA)
  - Electrocatalyst activity and stability
  - Electrocatalyst and gas diffusion layer (GDL) carbon corrosion
  - GDL hydrophobicity
- Develop and apply methods for accelerated and off-line testing

### Technical Barriers

This project addresses the following technical barrier from the Fuel Cells section (section 3.4.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability

### Technical Targets

2010 and 2015 Target: Durability with cycling:  
5,000 hours

### Accomplishments

- Durability testing simulating PEM fuel cells with shut-down/start-up cycling
- Measurement of operating conditions' effects on cathode carbon corrosion due to shut-down/start-up
  - Relative humidity (RH) effect
  - Purge rate effect
  - Temperature effect
- In situ characterization of MEAs by polarization curves, electrocatalyst surface area measurements, and high frequency resistance
- Post-characterization of tested fuel cell components by X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and contact angle measurements
- Off-line durability testing of fuel cell components
  - Potential cycling evaluation of electrocatalysts
    - Comparison of catalyst cycling protocols
      - H<sub>2</sub>/air vs. H<sub>2</sub>/N<sub>2</sub> cycling
      - Step potential vs. sweep potential during cycling
  - Environmental aging of components
  - Membrane accelerated testing at open circuit voltage (OCV)
    - RH effect on H<sub>2</sub> crossover, fluoride emission rate and OCV decay



### Introduction

In this project, LANL identifies and quantifies factors that limit PEM fuel cell durability by measuring property changes in fuel cell components during long-term testing. LANL also develops and applies methods for accelerated and off-line testing. The overall objective is to meet the 2010 and 2015 DOE target of 5,000 hours of durability with cycling. This report describes our Fiscal Year 2008 technical progress in characterizing and quantifying the durability of fuel cell components and their degradation mechanisms to support the DOE target of 5,000 hours of durability.

## Approach

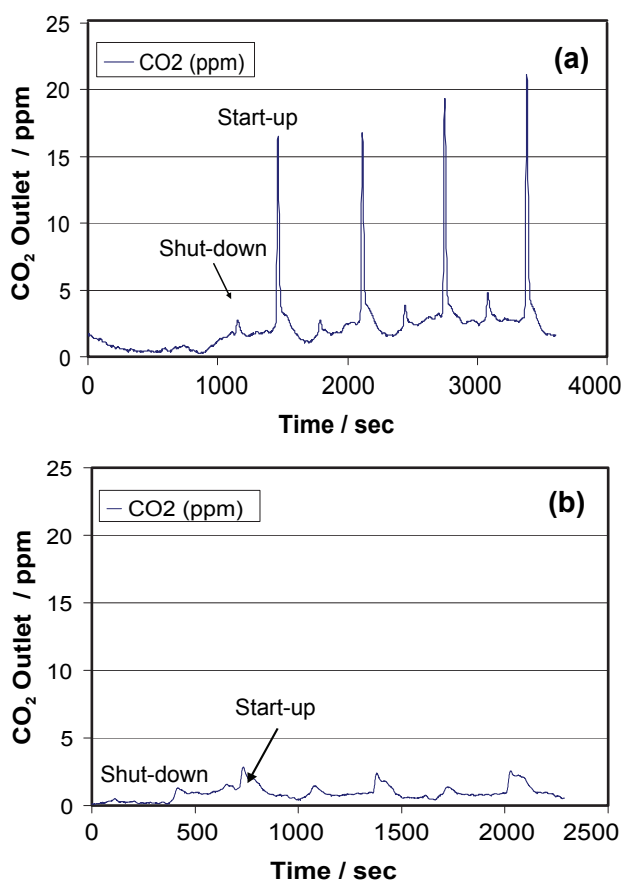
Our approach to understanding PEM fuel cell durability is to define degradation mechanisms, which will enable the design of improved fuel cell materials and components. This approach also helps to define operating conditions that promote degradation, which can lead to the design of operational procedures that improve durability.

Tests are conducted with steady-state conditions (both constant voltage and constant current) and with dynamic conditions using power cycling to simulate a vehicle drive cycle. Measurements of polarization curves, membrane resistance, hydrogen crossover and electrochemical surface area are made in situ to characterize those fundamental properties changing as a function of time. Available characterization techniques (including SEM/energy dispersive X-ray spectroscopy, XRD, XRF, X-ray photoelectron spectroscopy, and TEM) are used to characterize changes in the membranes, gas diffusion layers and catalyst after durability testing. Porosimetry measurements are used to help define structural changes in material properties. Contact angle measurements are used to monitor material hydrophobicity/hydrophilicity changes of materials. Accelerated testing techniques are used to help differentiate the contributions of individual fuel cell components to the degradation of the overall performance and hasten evaluation of new materials.

## Results

### Measurements of Degradation During Shut-Down/Start-Up Tests

Fuel cell catalysts have been shown to degrade during shut-down/start-up due to the formation of local potentials which can approach 1.5 V during the purging of hydrogen at the anode with air and with the subsequent introduction of hydrogen at start-up [1]. These local potentials create a condition under which the cathode catalyst degrades due to carbon corrosion. Measurement of carbon corrosion by non-dispersive infrared from the cathode is shown in Figure 1 during three shut-down/start-up cycles for two different anode purge rates. Measured CO<sub>2</sub> production shows that increasing the anode purge rate decreases the carbon corrosion due to less time at localized high potentials. Integration of the CO<sub>2</sub> peaks in Figure 1 yields the total amount of CO<sub>2</sub> produced during the shut-down/start-up event. When the anode purge rate was increased by ~4x (from Figure 1a to 1b), the carbon corrosion decreased during start-up by ~3x, while the decrease during shut-down was ~2.6. The non-linearity of the carbon corrosion suggests that the anode purge rate does not linearly effect localized potentials.



**FIGURE 1.** Anode purge rate effect during stop-start cycling on carbon corrosion with (a) Purge time (1 turn-over) = 15.0 sec (Anode:Flowrate: 100 sccm H<sub>2</sub>, Purge: 50 sccm Air) (b) Purge time (1 turn-over) = 3.7 sec (Anode: Flowrate: 400 sccm H<sub>2</sub>, Purge: 200 sccm Air). 50 cm<sup>2</sup>, 25°C

In Figure 2 we see that an increase in humidification level increases the amount of carbon corrosion during start-up. However, the inverse is true during shut-down, as the carbon corrosion decreases with increasing RH, although with less magnitude. In comparing the overall effect of water on the carbon corrosion rate, the amount of CO<sub>2</sub> production is much greater with the presence of water, than without (compare Figure 2 with Figure 1). A 5x increase in carbon corrosion is measured for similar purge conditions wet vs. dry for shut-down ( $4.9 \times 10^{-7}$  vs.  $1.0 \times 10^{-7}$  moles of CO<sub>2</sub>). While there was no detectable CO<sub>2</sub> for starting up dry at 80°C, this can be compared with  $1.8 \times 10^{-6}$  moles with humidified gases, which is larger carbon corrosion than observed for comparable conditions during shut-down.

### GDL Hydrophobicity Changes

We previously have shown that GDLs lose hydrophobicity during operation in fuel cells by measuring single-fiber Wilhelmy and sessile drop contact angles [2]. As the aggressiveness of the aging conditions was elevated, the contact angles decreased, i.e. the GDLs

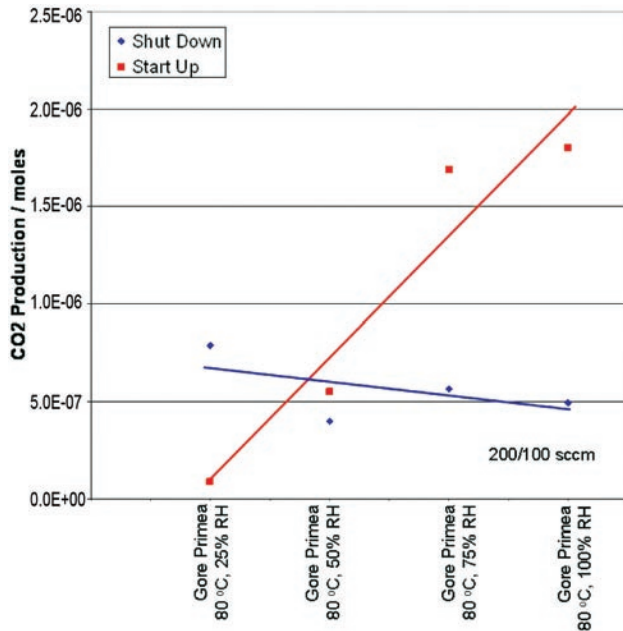


FIGURE 2. Amount of CO<sub>2</sub> produced during shut-down and start-up of a W.L. Gore™ Primea® series MEA as a function of humidification level. Anode/cathode flowrates of 200/100 sccm and 80°C.

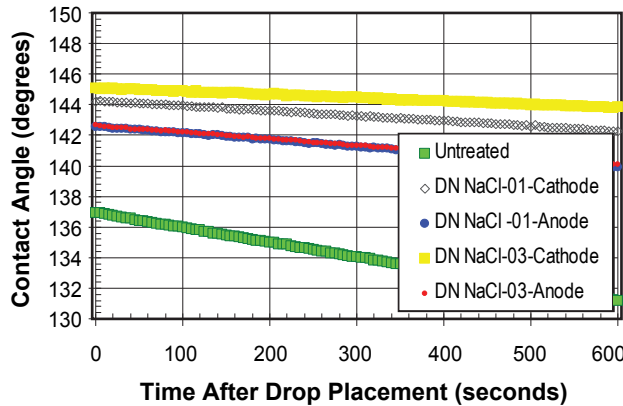


FIGURE 3. Contact Angle Changes of GDL after Exposure to NaCl

showed loss of hydrophobicity. Figure 3 shows dynamic sessile drop measurements for GDL materials before and after testing with NaCl during fuel cell operation. While in previous experiments GDLs lost hydrophobicity with aging, exposure to NaCl makes GDLs more hydrophobic. The exposure to NaCl also slows the rate of water uptake, as evidenced by the decreased slope of the contact angle measurement versus time.

### Membrane Degradation Tests at OCV

The degradation rate and mechanism of catalyst coated Nafion® 212 membrane was investigated at a series of RHs while holding the MEAs at OCV to

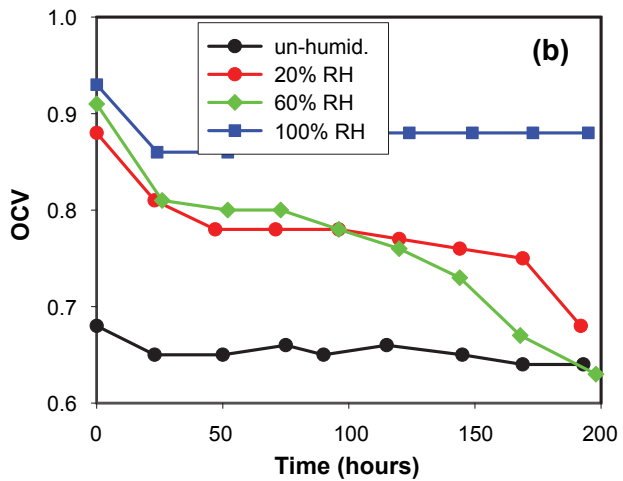
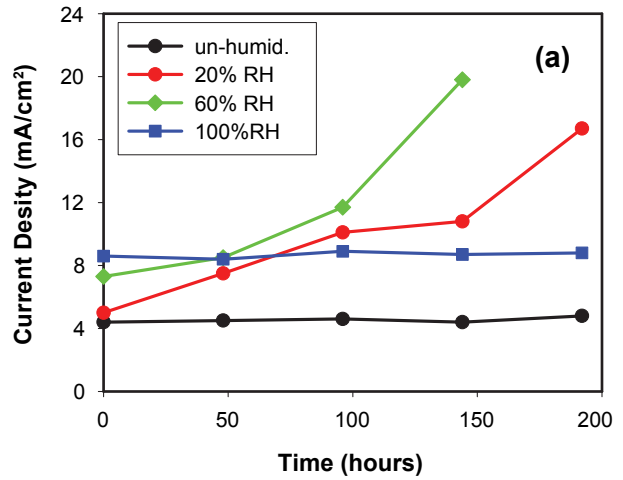


FIGURE 4. Gas RH effect on membrane degradation over time showing (a) hydrogen crossover and (b) open-circuit potential.

accelerate the membrane degradation. Figure 4a shows membrane hydrogen crossover with time for four different gas inlet humidities: 0, 20, 60 and 100% RH. Figure 4a shows at the un-humidified condition and at 100% RH, hydrogen crossover is constant, while at both 20% and 60% RH, hydrogen crossover increases significantly during the degradation test. Initially, hydrogen crossover at both 20% RH and 60% RH is less than that at 100% RH. However, hydrogen crossover reaches 19 mA/cm<sup>2</sup> after 144 hours at 60% RH and 14 mA/cm<sup>2</sup> after 192 hours at 20% RH. Therefore, at 60% RH, the membrane experiences the largest increase of hydrogen crossover during testing.

Figure 4b shows the OCV change with time during the same test as Figure 4a. The highest OCV was observed at 100% RH; an initial voltage drop occurred during the first period, after which the OCV was stable. The rate of OCV decrease was 0.25 mV/h. For an inlet RH of 60%, the OCV decreases significantly over the course of the degradation test, with a degradation rate

of 1.29 mV/h. At a lower RH of 20%, however, the degradation rate was 1.04 mV/h, which is slightly lower than that at 60% RH. At the un-humidified condition, the initial OCV is low, only 0.68V. Nevertheless, the OCV is steady during the entire test with a degradation test rate of only 0.20 mV/h. This is consistent with the previous observation that at 60% RH the membrane degradation proceeds at the highest rate.

Previous studies have concluded that lowering RH significantly accelerated the membrane degradation [3,4]. This conclusion may fit the change of OCV decay when the cell is operated at 100% RH compared to 60% RH, but does not explain the membrane degradation tendency when the RH was operated at 20%, particularly, at un-humidified condition. This apparent conflict occurs because previous RH-related membrane degradation studies were performed at two RHs (low or high), or in a small range of RH. There have been no reports on the change of membrane degradation in a full range of RH. This study shows that membrane degradation rate is low at both high and low RH. The highest membrane degradation rate may appear in the mid RH ranges (40-60% RH).

## Conclusions

Operational variables are important to component durability:

- RH, temperature, potential and potential cycling
- Shut-down/start-up variations important to electrocatalyst corrosion

Anode air purge during shut-down/start-up effects cathode catalyst corrosion:

- Anode purge rate influences the amount of cathode corrosion
- Increasing carbon corrosion is observed with increasing water content of the cell
- Carbon corrosion varies with temperature, RH, anode purge rate and shut-down vs. start-up

Hydrophobicity of GDL materials changes during operation:

- GDL hydrophobicity decreased with aging during operation
- GDL hydrophobicity increased after testing with NaCl

Membrane degradation is a function of operating conditions:

- OCV used to accelerate degradation
- RH influences the rate of membrane degradation

- Highest degradation rates observed at intermediate RHs

## Future Directions

Accelerated testing and durability correlation:

- Correlate accelerated durability tests to fuel cell performance
- Continue to develop accelerated tests for degradation mechanisms

## FY 2008 Publications/Presentations

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3. M. Inaba, T. Kinomoto, M. Kiriake, R. Umabayashi, A. Tasaka, and Z. Ogumi, *Electrochimica Acta*, **51**, 5746 (2006).
4. V. O. Mittal, H. R. Kunz, J. M. Fenton, *J. Electrochem. Soc.*, **153**, A1755 (2006).